Diversifying renewable feedstocks for new biobased polymers and applications

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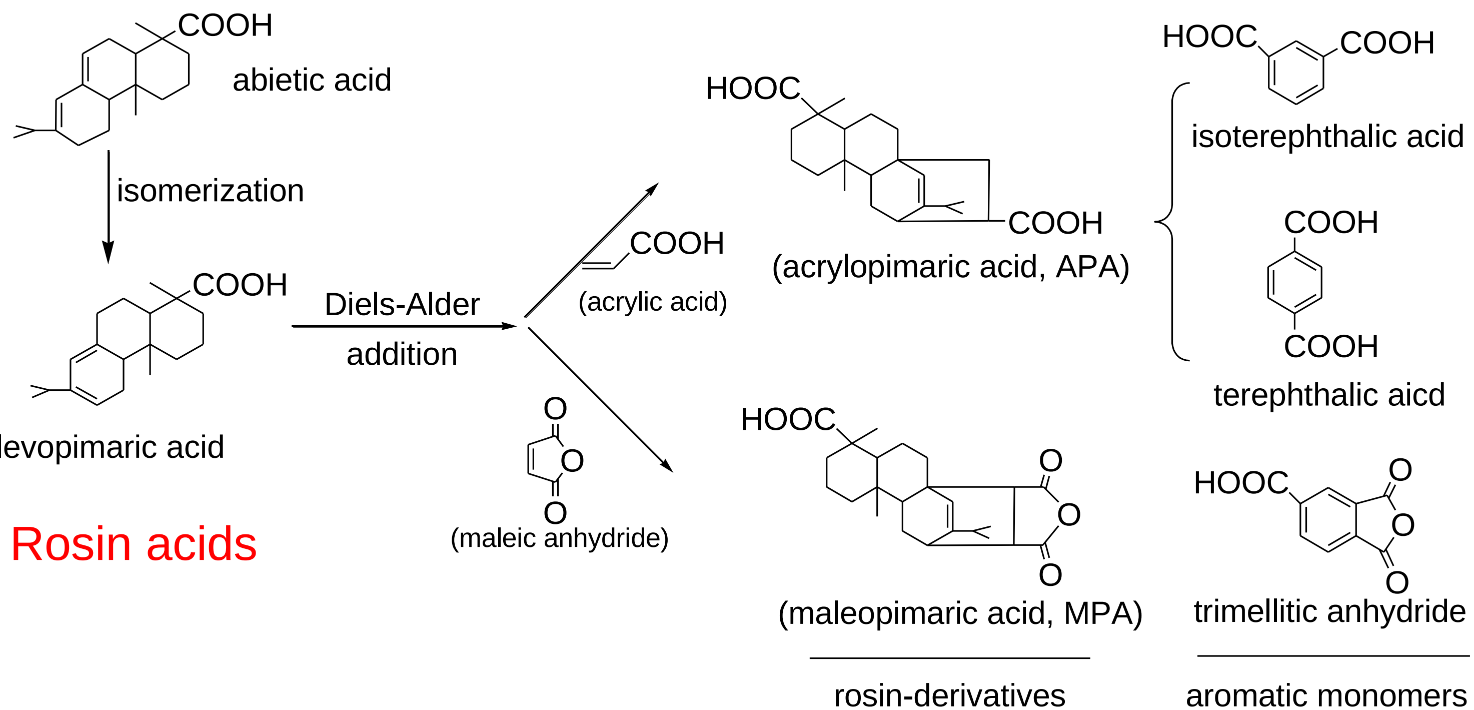
Bottlenecks of current biobased polymers

- Cost effectiveness
- Performance competitiveness
- Product diversity
- Availability
- Or all of above

New higher value polymers, new technologies and new applications are the solutions

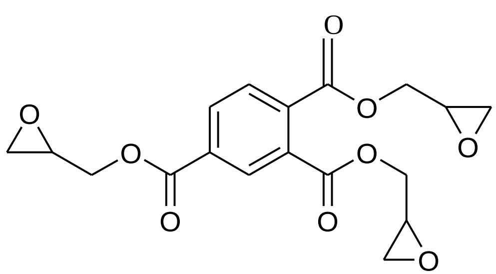
1. Rosin derivatives are promising alternatives to aromatic/cyclic building blocks for polymers



Rosin acids

Monomers for polyester powder coating

Curing agents for polyester-epoxy hybrid powder coating



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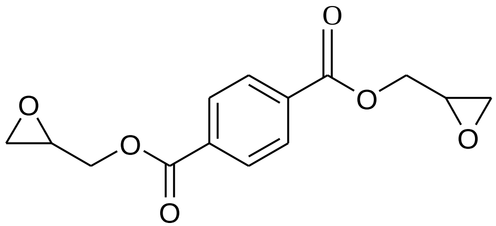
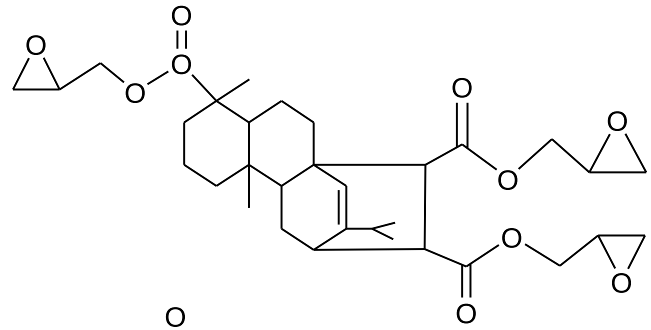


Structures of Araldite PT 910



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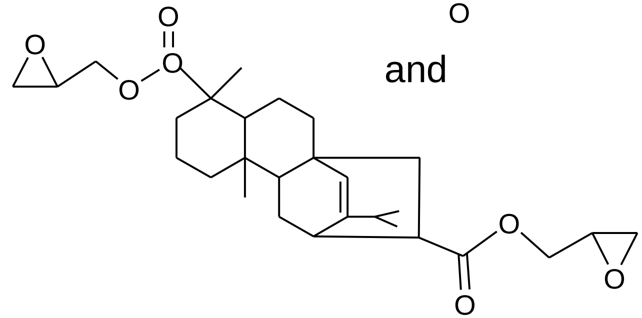
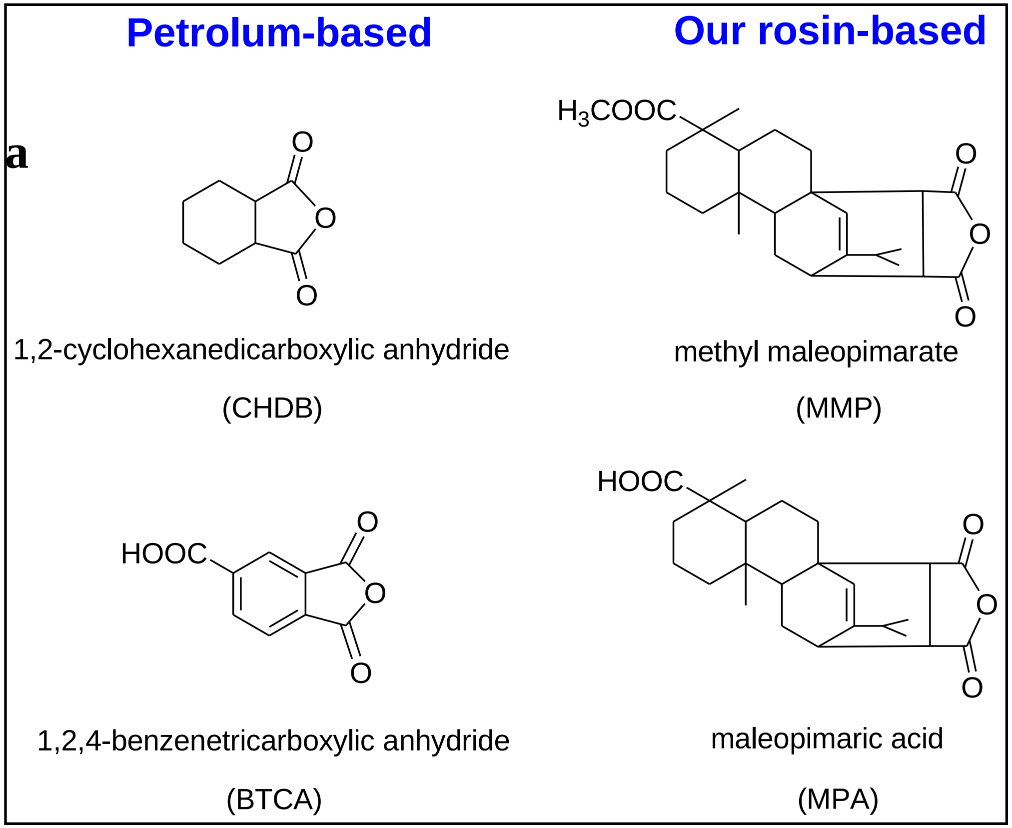
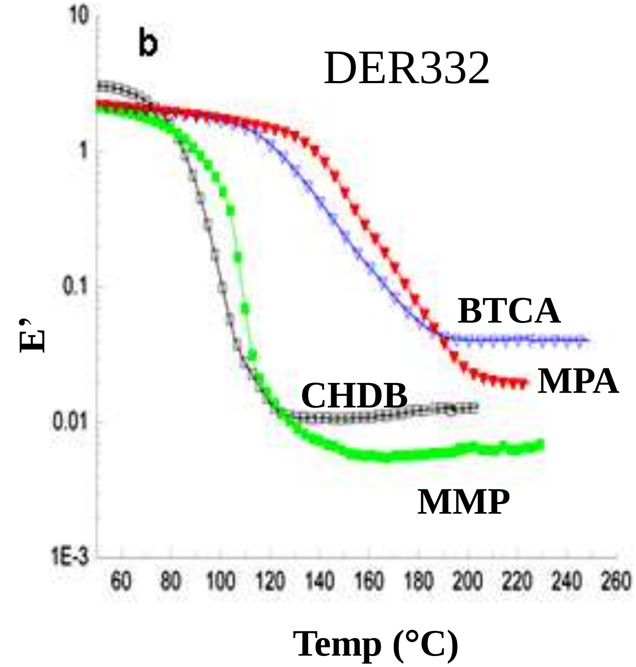


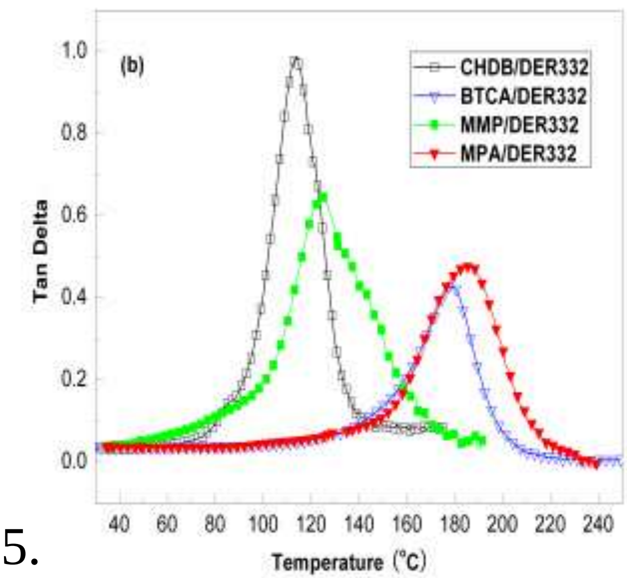
Structures of rosin-based curing agent

Rosin-based curing agent vs.
commercial curing agent Araldite PT 910

Rosin-based curing agents vs. petroleum-based counterparts

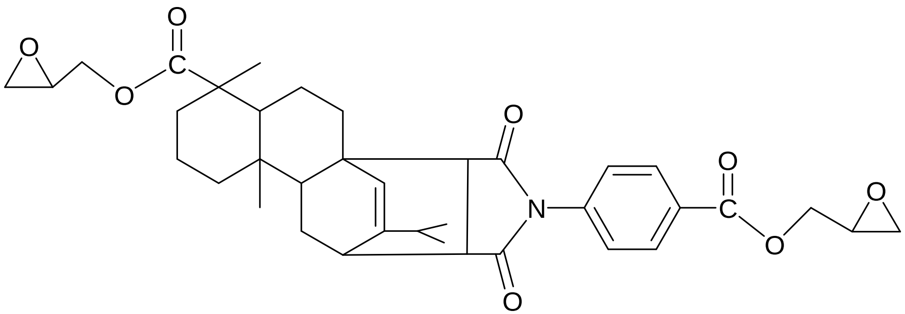




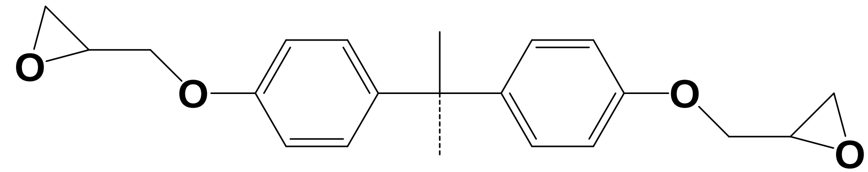


Liu & Zhang. *Green Chemistry* 2009, **11**, 1018 – 1025.

Rosin-based epoxy vs. petroleum-based epoxy



Rosin-based epoxy containing imide group



DGEBA

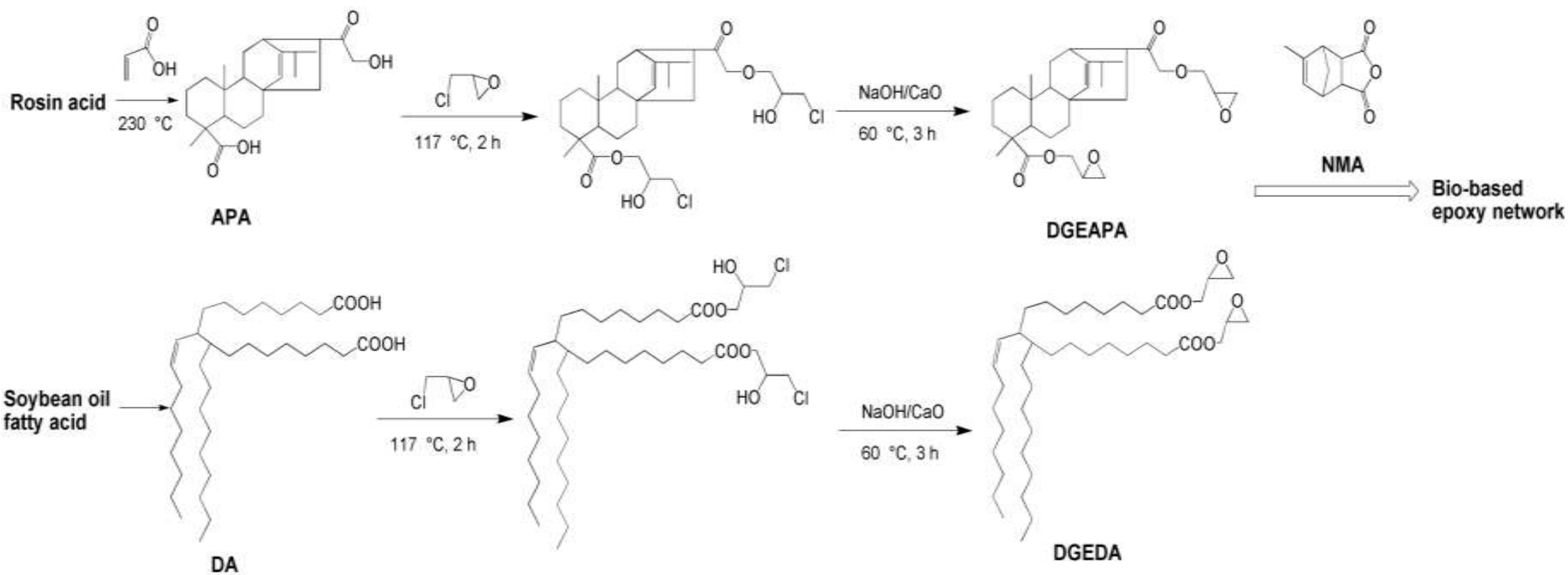
System	DMA (°C)		TGA (°C)
	T_g	G' (GPa, 30°C)	$T_{5\%}$[3]
R-epoxy[1]/CHDB	153.8	2.5	311
DER332/CHDB	144.3	3.3	330
ESO/TETA[2]	11.8	0.011	200 – 300

Epoxidized soybean oil

[1]Rosin-based epoxy; [2]Epoxidized soybean oil/triethylenetramine (data was adapted from Liu et al. 2005); [3]Temperature at 5% degradation

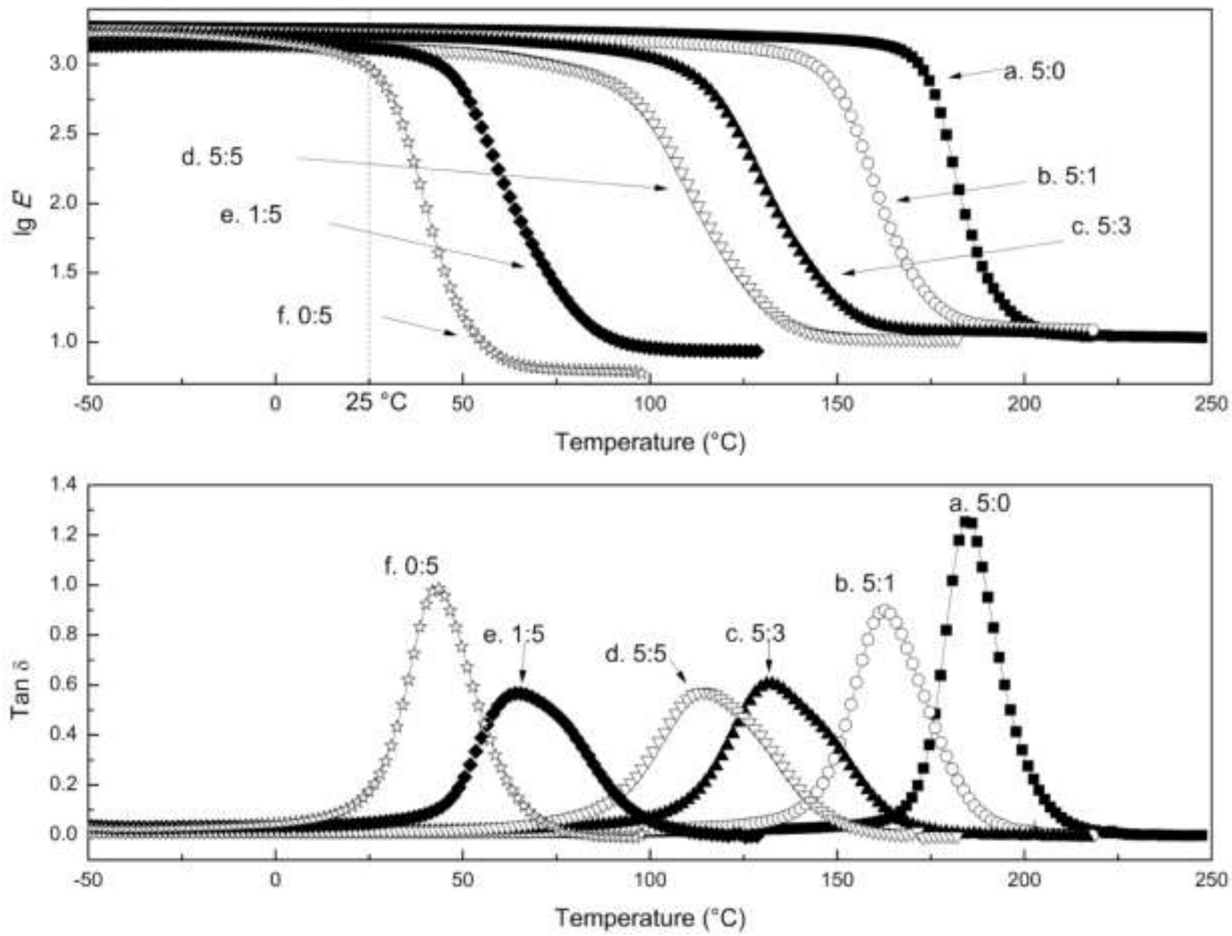
Liu & Zhang. *Polym. Int*. 2010, **59**, 607

2. New use of plant oil for polymer applications



Manipulate properties by combing plant oil-derived and rosin-derived resins

Effects of using mixed epoxies on dynamic mechanical properties

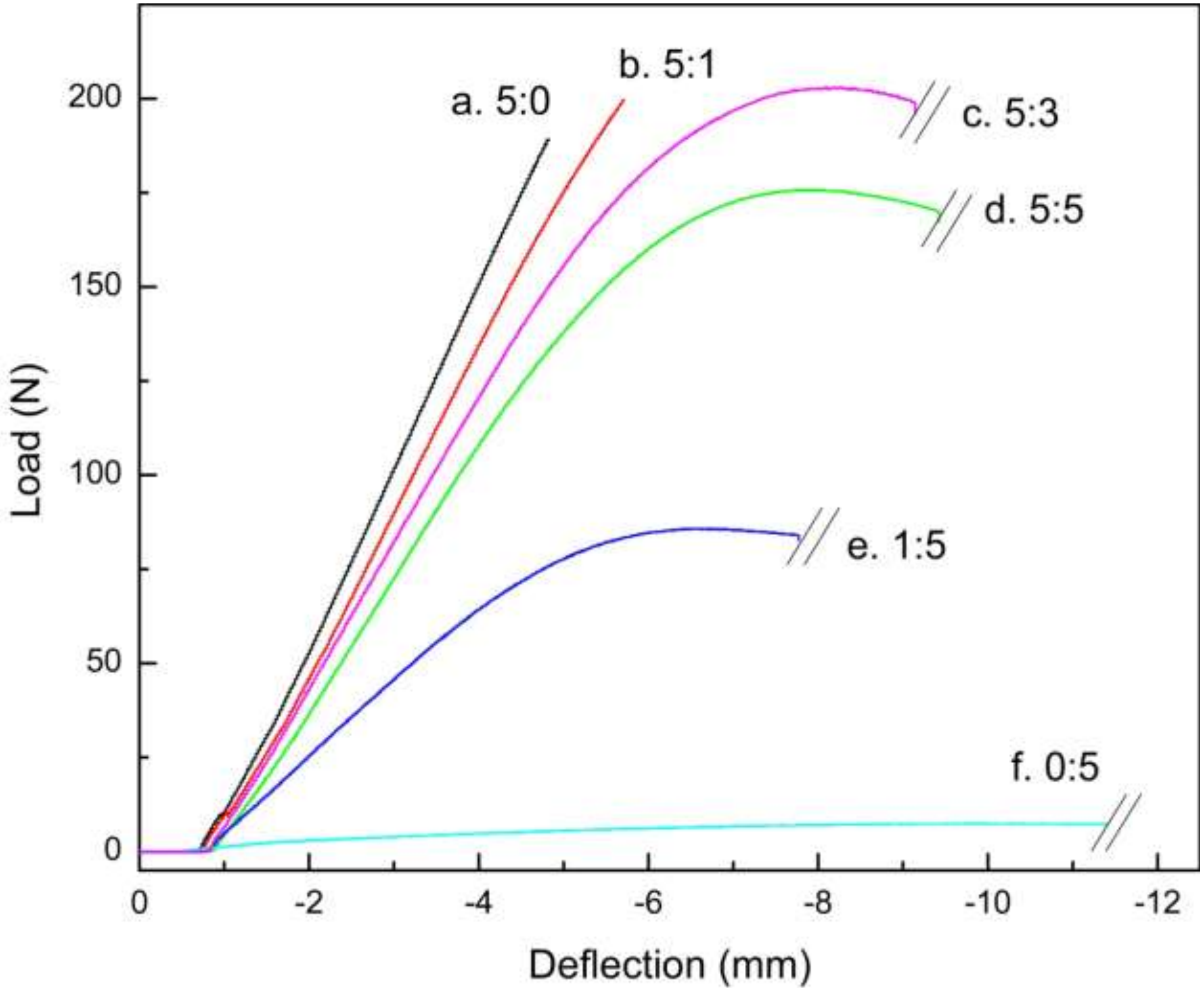


DGEAPA/DGEDA (rosin moiety/dimer acid moiety)

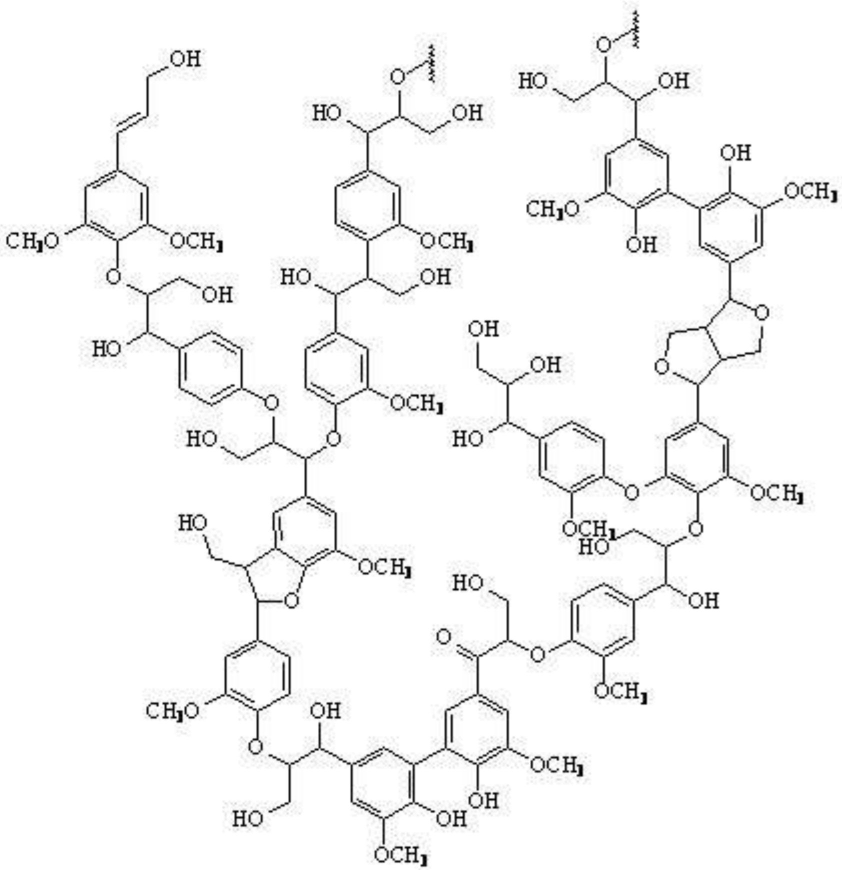
Increasing rosin-derived epoxy in the mixture

Flexural properties

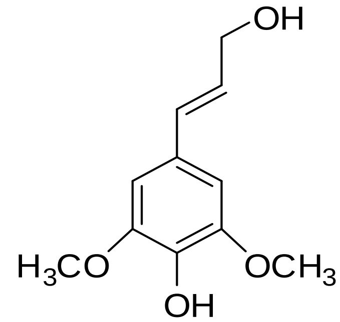
APADGE/DADGE



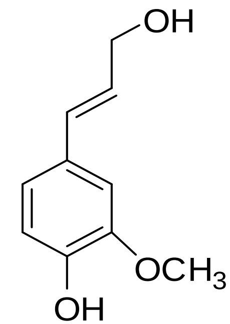
Lignin structure



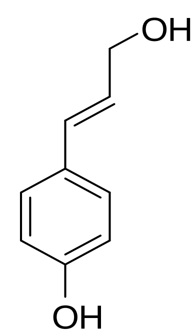
(http://www.research.uky.edu/odyssey/images/lignin.jpg)



Sinapyl alcohol



Coniferyl alcohol



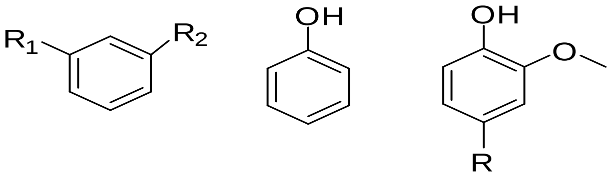
Paracoumaryl alcohol

Three monolignols

3. Utilization of lignin

- Fuel applications: short-term objective
  - Boiler fuel
  - Fuel additives via cracking and hydrogenation
  - Bio-oil through pyrolysis

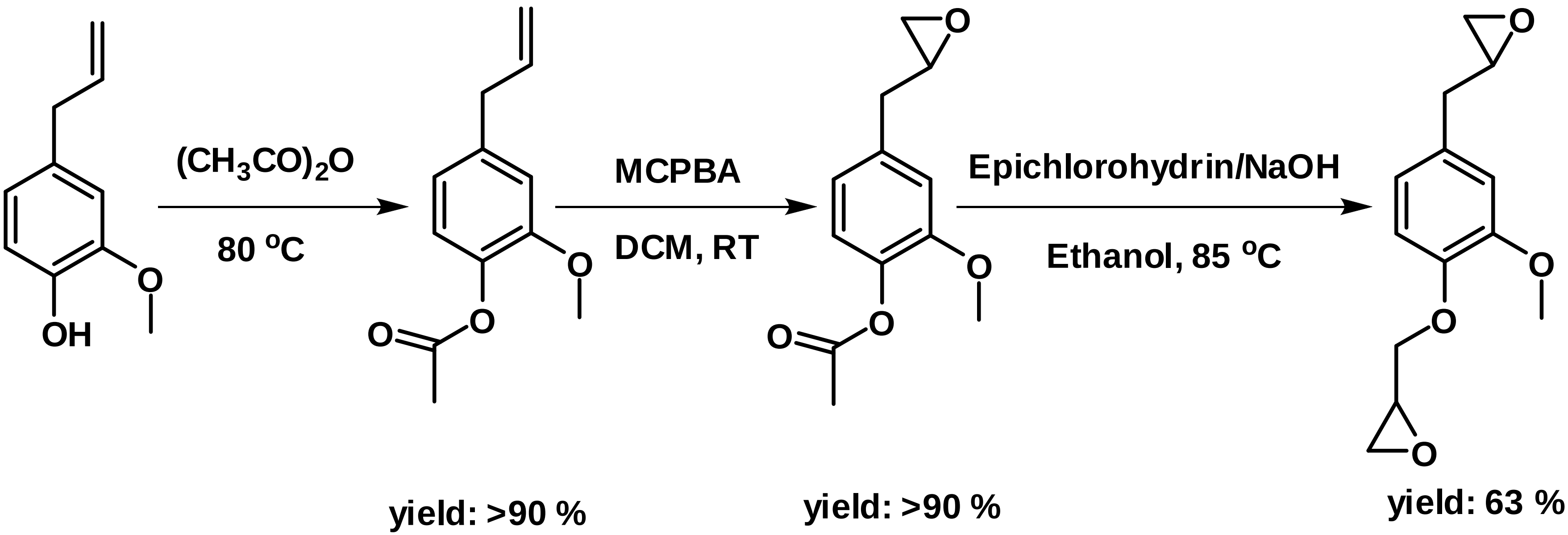
- Chemical applications: long-term objective
  - Aromatic chemicals
  - Substituted Cyclohexane
  - Cyclohexanone



$R_1, R_2 = H, CH_3$

- Polymer applications: mid-term objective
  - Comonomers & building blocks
  - Thermosetting resins
  - Carbon fibers
  - Fillers and additives

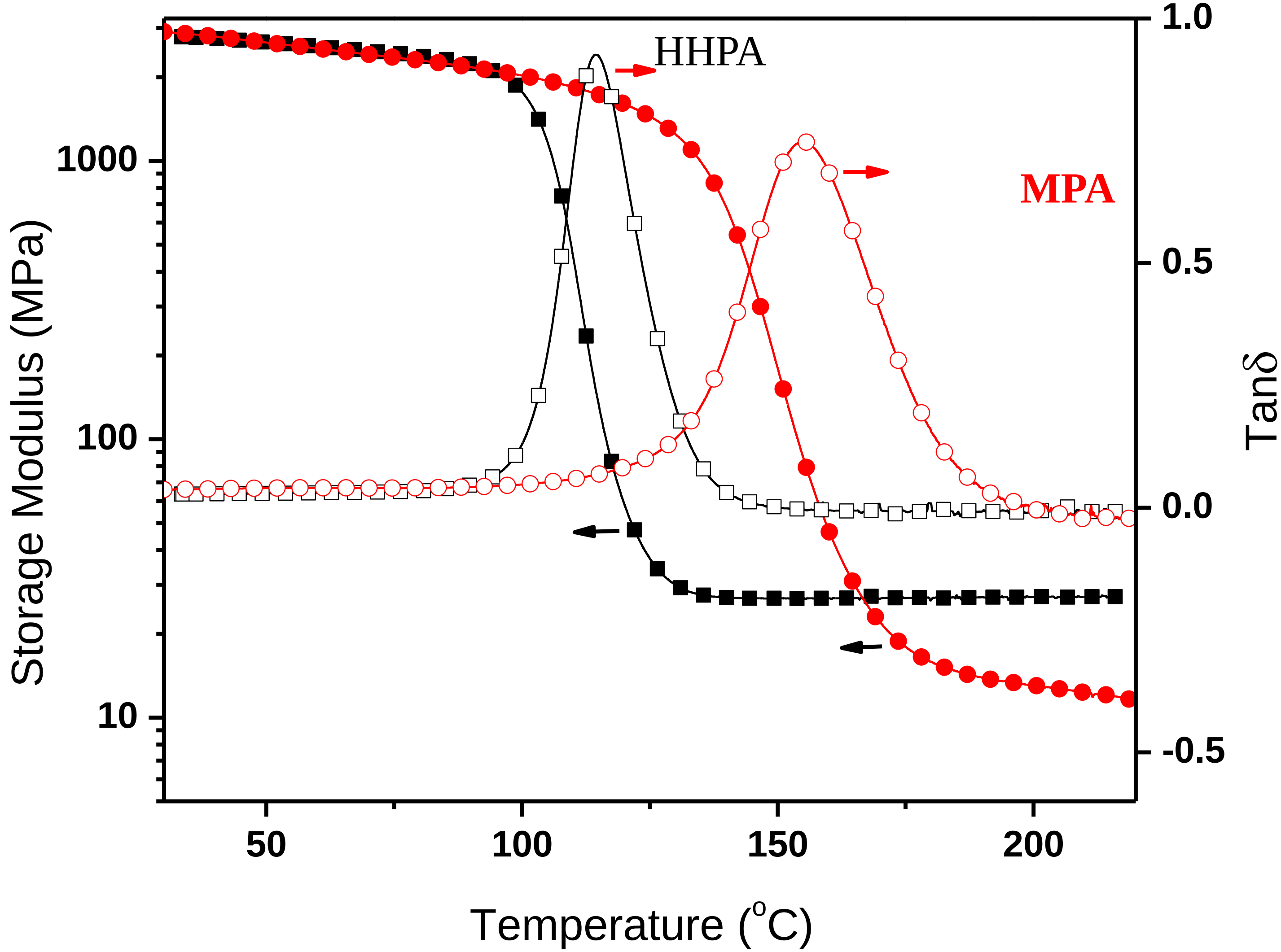
Scheme for preparation of epoxy from eugenol.



Euenol

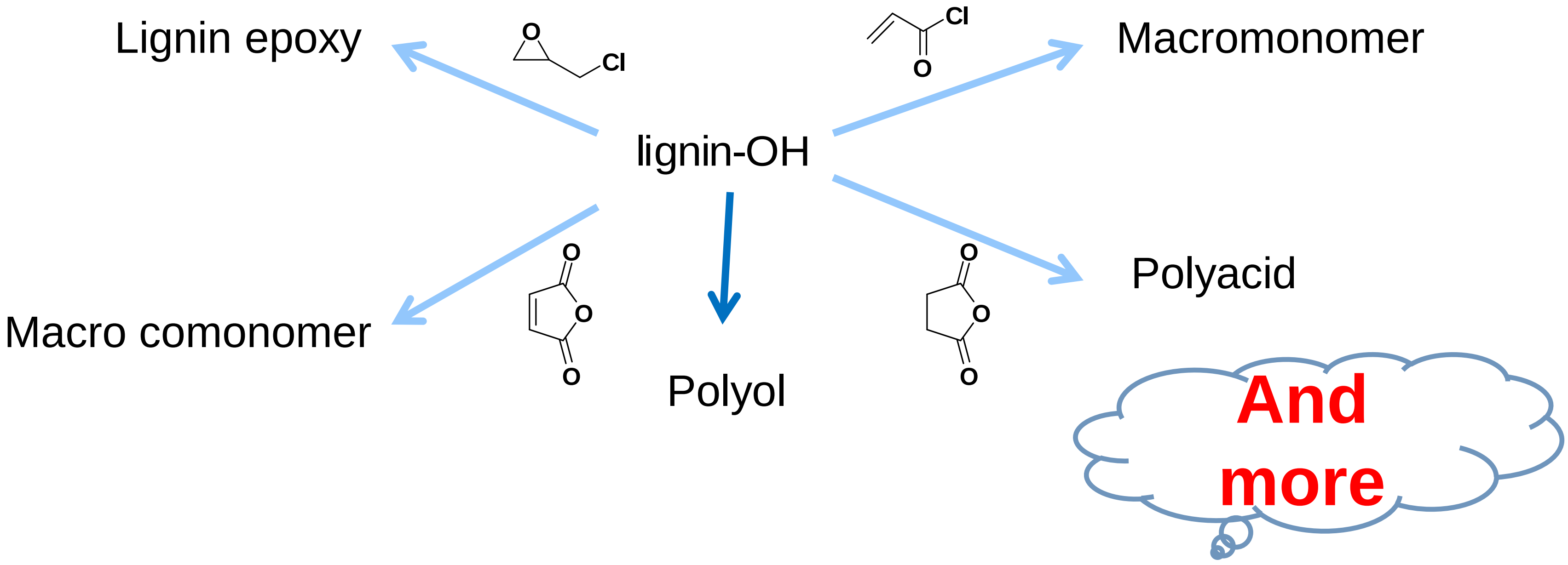
MPA cured epoxy

Euenol epoxy



Eugenol epoxy

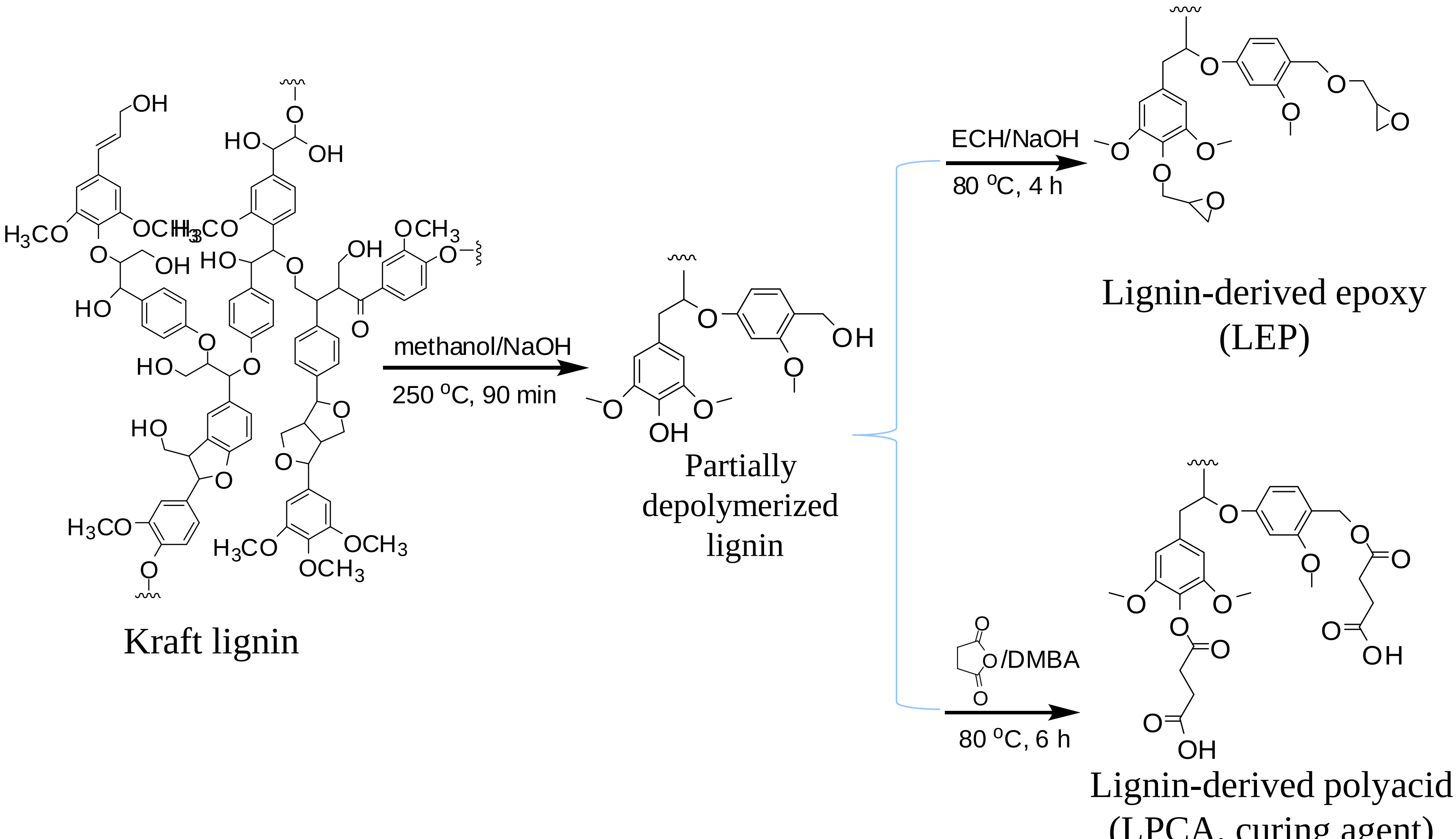
Direct modification of lignin or depolymerized lignin for polymers



Advantages & disadvantages

- Inexpensive
- Simple reaction

- Low solubility & functionality
- performance



Synthesis routes of lignin-derived epoxy and curing agent (PCA type)

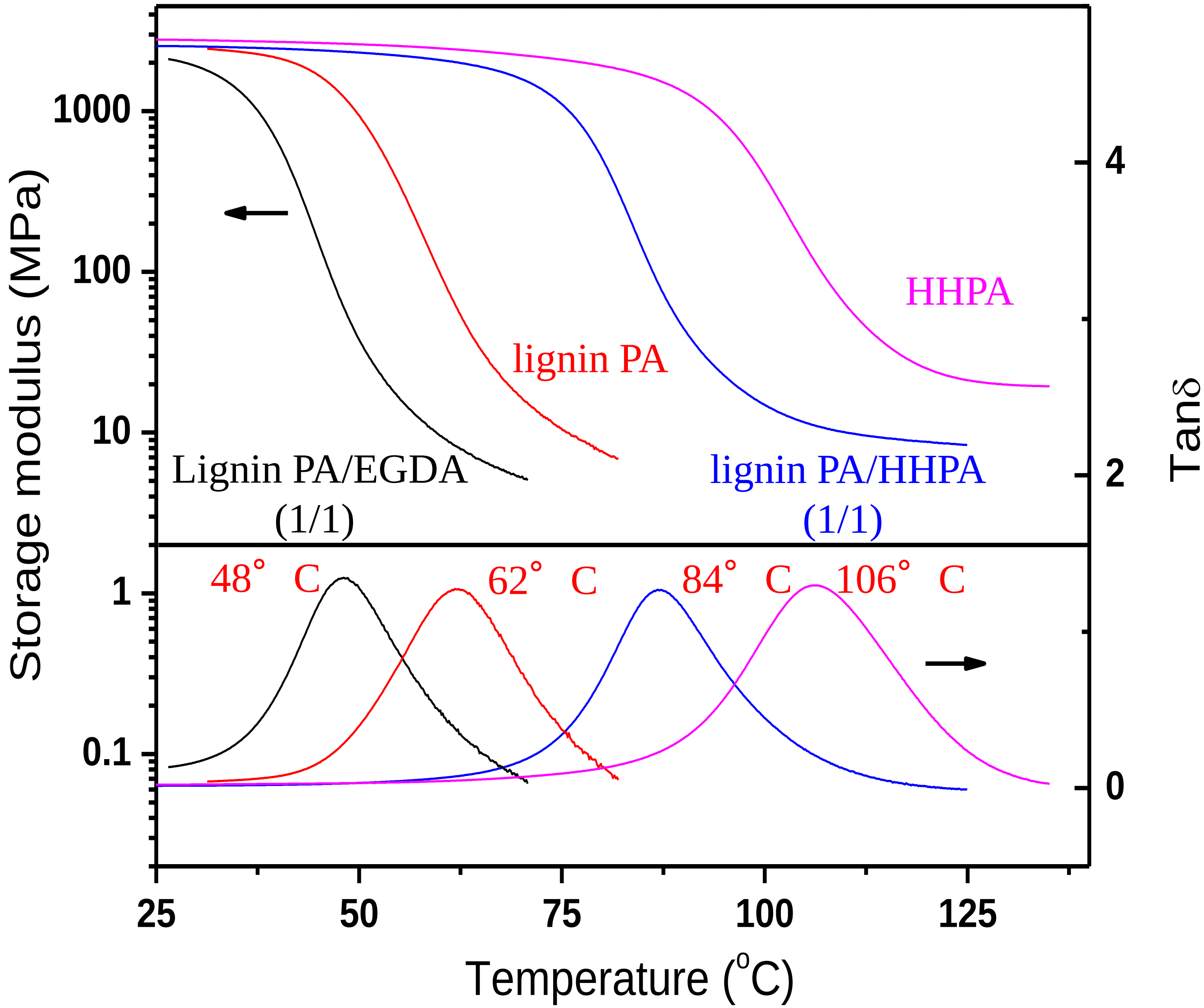
Kraft lignin (NJ23)

Cracked lignin

Lignin PCA
(as curing agent)

Lignin PCA cured
DER 353

Epoxy resins are high-value polymer products. In 2011, the world epoxy production was ~ 2.24 million tons (80 – 95% of which was bisphenol A epoxies).



DER 353 cured with different curing agents